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Influence of Process Conditions on the Physical Properties of TPS

Leon P.B.M. Janssen

A major challenge in the development of operational methods for the manufacture of products from thermoplastic starches is the use of classical polymer technology. The use of processes designed for synthetic polymers should make it possible to produce starch plastics that act as supplements to existing synthetic products [1, 2]. Moreover, similarity of production methods should facilitate the acceptance of thermoplastic starches in the plastics industry. Still, however, starch plastics have not yet become widely introduced as consumer goods, due to some major drawbacks. One of the main problems of starchy material is its brittleness. This brittleness is caused by the relatively high glass transition temperature (T_g) and a lack of the so-called sub-T_g mainchain relaxation areas [3]. On storage this brittleness even increases, due to retrogradation and volume relaxation processes. During the retrogradation process the starch recrystallizes; this process can be divided into two parts. The recrystallization of the amylose component is an irreversible and very fast process. However, the reversible crystallization of amylopectin is much slower, and retrogradation can be regarded as the long-term recrystallization of the amylopectin component [4]. This spontaneous recrystallization process is caused by the tendency of macromolecules to form hydrogen bonds with expulsion of trapped water molecules or other solvents [5]. Retrogradation and volume relaxation also cause another problem: namely shrinkage. Dependent on the processing technology, these phenomena can last for a few weeks, with total shrinkage of more then 10%.

The T_g or glass transition temperature is an important and measurable parameter giving information about the retrogradation behavior. Besides that, the T_g is also of great importance for the mechanical properties of the material. Beneath the glass transition temperature the material exists in an amorphous, "frozen" liquid structure with stiff and brittle behavior. Below its T_g the intermolecular bonds are not broken, due to the small amounts of room left for Brownian movement, as is stated in Eyring's "free volume theory" [6]. The specific volume increases relatively slowly with increasing temperature. When the material is heated up, at temperatures close to T_g the cohesive forces decrease drastically, the polymer expands, and the free volume increases to such an extent that there is

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room for migration of segments containing about 20 to 40 monomer units. The polymer now starts to flow, its characteristics being determined by the temperature increase above T_g and the crystalline structure, if any. The free volume is equally distributed throughout the material and in an unperturbed state the movements of the segments are random. However, when an external stress is applied, the segment migration will no longer be random but will occur in the direction that tends to relieve the applied stress, so the polymer will show a rubbery behavior. A sub-T_g (a glass transition temperature occurring at a lower temperature than expected) is in general of great importance for the product quality.

Starches from different sources, such as waxy maize, wheat, potato, and pea starch, behave differently when extruded with the plasticizer glycerol, this in concentrations of 15, 20 and 25% (w/w). De Graaf *et al.* [2] measured the glass transition temperatures of the resulting thermoplastic products by Dynamic Mechanical Thermal Analysis (DMTA). As well as their mechanical and structural properties, the transition temperatures of the materials during tensile and impact tests were also evaluated. Above certain glycerol contents, depending on the starch source, a lower glass transition temperature (T_g) resulted in decreased moduli and tensile strengths and increased elongations. Lowered T_g vales at different glycerol contents did not influence the impact strength. When the amylose/amylopectin ratio was increased a decrease in T_g was found. For pea, wheat, potato, and waxy maize starch the T_g values are 75 °C, 143 °C, 152 °C and 158 °C, respectively. This leads to the viewpoint that products with higher percentages of amylose are more flexible. The shrinkage of the specimens effected by injection-molding can be considerably higher than that produced in specimens made by pressing. The strength of the glassy polymer is that it offers the capability to dissipate energy in situations of shocks on short timescales, so the polymer is less brittle. A sub-T_g can be caused by the release of limited motion potential in parts of the main chain or lateral groups or it can be caused by the presence of a second, smaller polymer. Sub-T_gs always occurs at lower temperatures than main T_gs. Addition of plasticizers such as water, glycols, sugars, and amides will lower the T_g and therefore make the thermoplastic starch more rubber-like.

8.1 Plasticizers

Plasticizers act by spacing out the molecules and reducing interactions. Efficient plasticizers generally have low viscosities and low temperature coefficients of viscosity. This is to be expected from theories of T_g based on free volume concepts because free volume and viscosity are related. A plasticizer is often a polymer with a low molar mass, and consequently a greater free volume. Because of this, polymer chains will have increased mobility and so the T_g will shift to a lower value, resulting in a less brittle polymer. An important requirement is that the plasticizer be perfectly mixed on a molecular scale, such that the plasticizer is homogeneously blended in the polymer, or the polymer in the plasticizer. The

resulting T_g of such a homogeneous mixture is given by the following equation [7]:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \tag{8.1}$$

where T_g is the glass-transition temperature of the blend, T_{g1} that of polymer 1, and T_{g2} that of polymer 2, whereas W is the weight fraction. Plasticizers may also serve another purpose: they decrease the melt viscosity. The lower the melt viscosity, the more easily can the material be processed or fabricated at lower temperatures. Furthermore, the plasticizer should have a high boiling point to avoid its evaporation during further processing and storage of the final product [8].

Besides plasticizer features, properties of the starch itself, such as the amylose/amylopectin ratio, also have an influence on the final material. As mentioned above, amylose and amylopectin recrystallize in different ways. Amylose will form the more crystalline part of a thermoplastic and amylopectin the amorphous component; the opposite behavior is found in the native starch granule, in which amylopectin is predominantly the crystalline part. The source of the starch determines the ratio and the molar mass distribution of amylose and amylopectin, and consequently the properties of the thermoplastics made out of it [7]. In this chapter the effects of and relations between the plasticizer, the amylose/amylopectin ratio, and the mechanical properties of four starches from different sources – potato, pea, wheat, and waxy maize – are described and discussed. Besides an overview of the properties, this should finally lead to better insight into the behavior of starch materials during processing.

8.2 Extrusion of Thermoplastic Starch

Thermoplastics are extruded from four starches together with different amounts of glycerol. The potato starch used (Avebe, Veendam, the Netherlands) is food grade and has a moisture content of 13% (w/w). The pea starch, from Parrheim foods (Manitoba, Canada), is also food grade and contains 9% (w/w) moisture. Cerestar Benelux BV (Sas van Gent, the Netherlands) supplied the waxy maize starch, with 9% (w/w) moisture. The wheat starch was supplied by Cerestar Germany (Krefeld) and contained 8% (w/w) moisture. The amylose/amylopectin ratios (information obtained from the starch suppliers) of the starches are shown in Table 8.1. Starch was introduced into an intermeshing co-rotating twin-screw extruder (APV Baker MPF-50, Peterborough, UK) with a double, round die opening of 3 mm. The APV has a length/width ratio of 25 : 1 and consists of 10 heating sections. The screws were constructed with transport, kneading (30°), and pressure elements in the following order: 9D transport – 1D kneading – 5D transport – 2D kneading – 3D transport – 5D pressure. Glycerol (0.3% w/w water and technical grade, Chemproha, Dordrecht, the Netherlands) was added 10 cm

Table 8.1 Extrapolated glass transition temperature and related amylose/amylopectin ratios of the starches used, according to de Graaf [9] and Whistler *et al*. [10].

Source of origin	T_g extrapolated from Figure 8.2 (°C)	Amylose/amylopectin[a]
pea	75	2:1
potato	152	1:4
wheat	143	1:4
waxy maize	158	1:99

a Information from starch suppliers.

downstream from the starch feed. The starch was gelatinized by use of a screw speed of 110 rpm and a linearly increasing wall temperature varying from 45–150 °C from the feed zone to the die. The processed material was subsequently chopped to provide granulate, after which test specimens were produced by injection-molding and pressing. In the case of the pea starch an extra amount of water (~10% with respect to the starch throughput) had to be added, to avoid degradation during extrusion. The obtained products were immediately packed in airtight bags and stored in dark, cool surroundings. The products were analyzed within two days.

8.3 Test Methods

Specimens, shaped according to ASTM-D 638, were prepared with an injection-molding machine from Arburg BV (Nieuw-Vennep, the Netherlands) (Allrounder type 221-55-250). The injection-molding temperatures were 150 °C. The obtained products were immediately packed in airtight bags and stored in dark, cool surroundings. The water contents of most of the test specimens used varied only a little, around 9–10% w/w moisture, although in the cases of pea and potato starch higher moisture contents were found (around 12–13% w/w). An Instron Corporation model 4301 machine (Canton, Massachusetts) with clamps of 5.0 kN, operating at a grip distance of 23.0 mm and a crosshead speed of 10.0 mm min^{-1}, was used for tensile tests. At least five specimens of each type of material were tested. Impact tests were done with specimens, unnotched according to ASTM-D 256-56, which were made on a press at ±150 °C under 30–103 N m^{-2}. The unnotched type was used because of the brittleness of some materials, which made notching impossible. A Cantilever Beam (Izod type) impact machine from Zwick Materialprüfung with hammers exerting an impact from 0.5–4.0 J was used for the impact tests. Unnotched specimens of some synthetic polymers (PS, PP, LDPE, and HDPE) were also tested for comparison. At least ten specimens of each material type were tested

8.3.1
Dynamic Mechanical Thermal Analysis (DMTA)

Dynamic Mechanical Thermal Analysis tests were used to measure the glass transition temperatures of the batches. With this technique the modulus of a polymer can be monitored against the frequency of an oscillating deformation of a sample bar at different constant temperatures. For a viscoelastic polymer two moduli can be distinguished: a storage modulus (E'), which is related to recoverable elastic energy stored in the sample, and a loss modulus (E''), related to deformation energy dissipated as heat of friction. Both moduli show decreases around the glass transition temperature and the dissipation factor (damping), $\tan\delta = E''/E'$, will give a peak around phase transitions. The temperature at which this occurs is referred to as the glass transition temperature [11] Actually, the conventional T_g is 5 to 15 °C higher then the temperature of maximum damping [12]. The analyzer used was from Rheometric (Piscataway, NJ, type: Solids analyzer RSA II). The specimens were made by pressing and each had a width of 6 mm and a thickness of 1.5 mm. During testing, the temperature of each sample was raised by 2 °C min^{-1} and the angular frequency was 6.28 rad s^{-1}.

8.4
Glass Transition Temperature

The influence of the amylose/amylopectin ratio and the amount of glycerol on the glass transition temperature (T_g) was determined by comparing the results for thermoplastic starches produced from various sources and with three different glycerol percentages (15, 20 and 25%, w/w). Figure 8.1 shows broad tanδ peaks for starches with 15% glycerol. The products with 20 and 25% glycerol, not illustrated, show comparable characteristics. The existence of a broadened transition region diminishes the temperature sensitivity of the mechanical material properties. This broadening is caused by heterogeneity [12] in the tested material and decreases with increasing glycerol content and increases with increasing amylose/amylopectin ratio (Figure 8.1). This means that a certain level of heterogeneity exists between amylose and amylopectin, so the glycerol acts not only as a plasticizer but also as a solvent in which both amylose and amylopectin dissolve, forming a more homogeneous mixture. After the T_g has been passed the measurement is no longer smooth. High-amylose starch (pea) will break down less quickly than high-amylopectin starch (waxy maize), indicating increased temperature processibility of the former. The temperature region between the T_g and the flow point will thus increase for materials containing higher percentages of amylose. This difference in heat resistance can be attributed to the irreversible retrogradation of amylose, in contrast with the reversible retrogradation of amylopectin. The initial rate of development of stiffness of starch gels after gelatinization is dependent on the botanical source and the degree of solubilization of amylose during gelatinization. This initial crystallization is not reversed on heating to 100 °C.

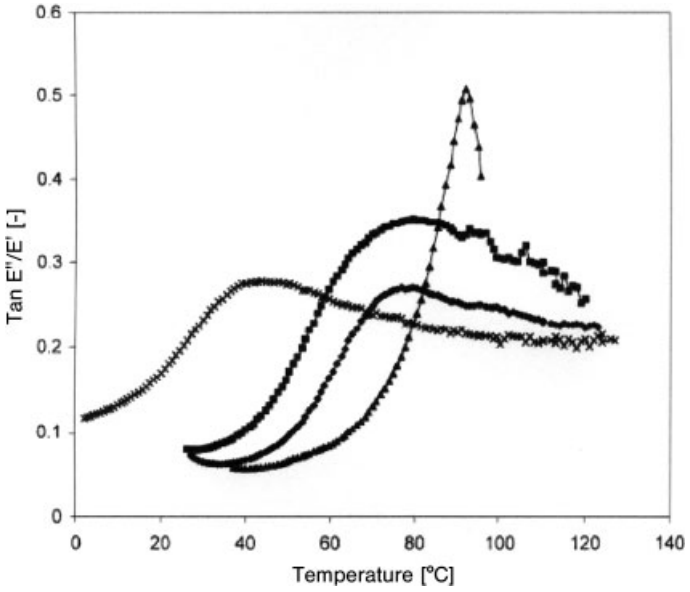

Figure 8.1 Plots of DMTA tests for potato (♦), wheat (■), waxy maize (▲), and pea starch (×) with 15% glycerol content.

However, there is also a long-term increase in gel stiffness, which is thermally reversible below 100 °C and can be attributed to amylopectin crystallization [13]. This is why waxy maize can be processed at lower temperatures than pea starch, because it is already in a flowing state at lower temperatures.

Figure 8.2 shows glass transition temperatures as a function of glycerol content. It is clear that the T_g values decrease in the order waxy maize > wheat > potato > pea starch and, with regard to the glycerol content, in the order 15% > 20% > 25%. Products containing higher levels of amylopectin (waxy maize) have higher T_g values than materials with less amylopectin (pea). The lower molar mass of amylose and its lack of branches results in a greater free volume of pea starch, so that (parts of) the chains can move more easily. This explains the lower T_g of amylose in relation to the branched amylopectin, so materials with higher amylose weight fractions will give lower T_g values. It can be expected from Equation 8.1 that glycerol should lower the transition temperature. Characteristically, the T_g of an undiluted polymer is much higher than that of a typical low-molar-mass, glass-forming diluent. As the diluent concentration of a solution is increased, the T_g decreases monotonically, because the average molar mass of the homogeneous polymer/plasticizer mixture decreases, and its free volume increases [13]. The small plasticizer molecules make chain movements easier. The greatest effect of glycerol is seen for waxy maize, so glycerol has a greater impact on materials containing more amylopectin. This effect can be explained by the fact that the T_g values of amylopectin and glycerol are more different from each other than those

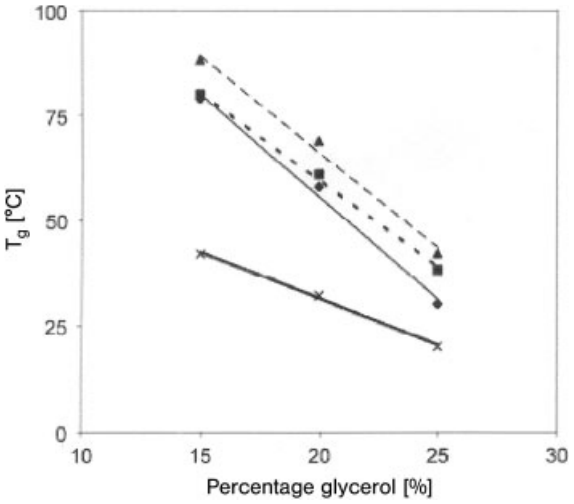

Figure 8.2 Glass-transition temperatures of potato (♦), wheat (■), waxy maize (▲), and pea (×) starch as a function of the glycerol content. The drawn lines are trend lines.

of amylose and glycerol. Extrapolation of the glycerol contents in the starch mixtures to zero results in approximations to the T_g values of the pure starches. These T_g values are listed in Table 8.1.

8.5 Tensile Strength

Figure 8.3 shows different stress/strain behavior as a function of the glycerol percentage and the starch source. For a low glycerol content (15%) the samples break in brittle fashion for potato, wheat, and waxy maize; for this last material the sample even fractures while the stress is still increasing. This occurred despite the fact that the glycerol reduced the T_g values of these materials relative to those of the pure starches; obviously these decreases were not sufficient to make them flexible. With higher percentages of glycerol (and in all cases for pea starch), a stress maximum is observed together with a clearly higher elongation. High glycerol levels decrease the stress, with the stress maximum becoming less dominant or not being observed at all. At a temperature of 20 °C and a low glycerol content the materials with higher amylopectin percentages are far below their T_g values. Therefore, their chain mobilities are very low and the samples show brittle stress/strain behavior. Pea starch, which has a much lower percentage of amylopectin, and therefore a lower T_g, is more flexible. At higher glycerol/starch ratios the starch chain mobility increases as the glycerol molecules weaken the interchain hydrogen bonding. The T_g is lowered, approaching the usage temperature. The starch chains

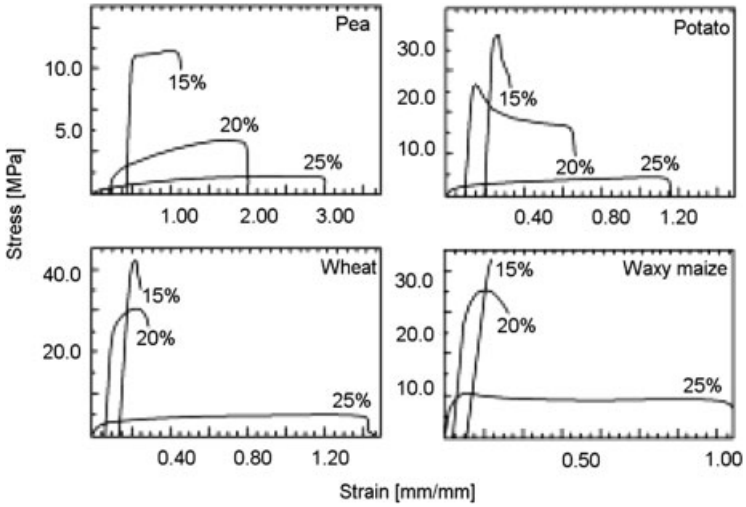

Figure 8.3 Stress/strain diagrams for potato, waxy maize, pea, and wheat starch.

can adapt to the applied stress and the possible elongation increases because the chain mobility is increased. If the T_g is lowered below 20 °C, no stress maximum is observed at all, because chain movements are again facilitated, leading to lower stress and greater elongation [6].

Figure 8.4 shows mean tensile strengths and elongations as functions of glycerol content for the four different sources of starch at 20 °C and 50% humidity. The courses of the moduli against glycerol content are not illustrated, as these are comparable to those of the tensile strengths. The moduli vary from 900 MPa for waxy maize with 15% glycerol to 7.3 MPa for pea starch with 25% glycerol. It is obvious that pea starch has a low tensile strength and modulus, which steadily decreases with increasing glycerol percentage. Besides that, the pea starch product shows a large elongation at break, as already observed in the plots. The relatively large content of linear amylose molecules means that the entanglement between the chains is not very strong, so they will slide easily along each other with low stress and large elongation. The maximum tensile strength and modulus, obtained with 15% glycerol, can be compared with that of LDPE (10 MPa), the elongation at break with that of polypropylene (250%). The starches of potato, wheat, and waxy maize became very brittle at low levels of glycerol (15%). This results in moduli between 700 and 900 MPa, comparable to that of HDPE, and tensile strengths around 35 MPa, which is equal to the value for polystyrene. The higher amylopectin contents mean that the chains, because of the branched structure, are less ordered and therefore have a greater degree of entanglement, causing brittle fracturing with higher stress. Glycerol gives the chains more mobility and because of this the interactions between the chains are lowered. This is the reason why the

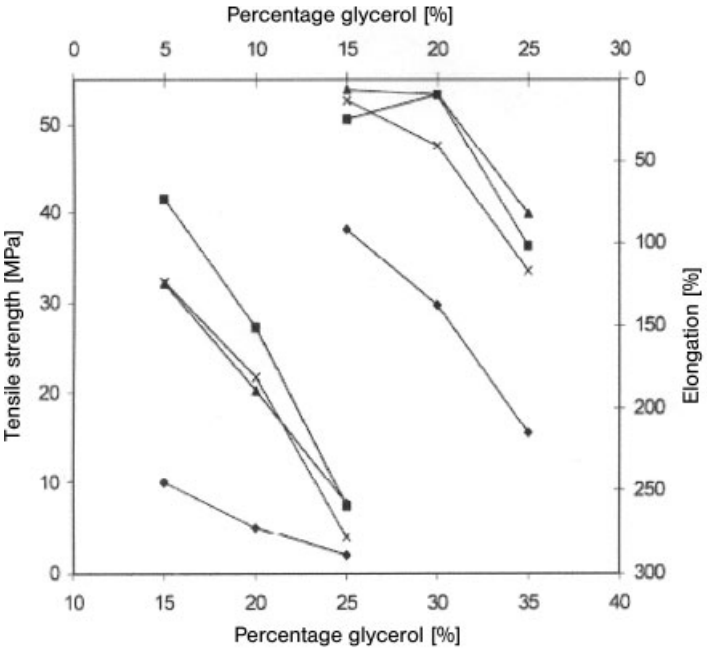

Figure 8.4 Tensile strength and elongation of potato (×), wheat (■), waxy maize (▲), and pea (♦) starch after 1 day as a function of glycerol content.

tensile strengths and moduli decrease and the elongations increase with increasing glycerol content. With regard to the tensile strengths, a smaller effect of glycerol is observed for pea starch, the high-amylose starch, than for the other starches with lower amylose contents. The difference in tensile strength between potato and wheat starch, in which the amylose/amylopectin ratios are nearly the same, can be explained by the difference in moisture content. The higher moisture level in potato (13%) relative to wheat (9%) will lower the T_g and consequently the tensile strength [14].

However, it is not directly explainable why the tensile strength of wheat starch is higher than that of waxy maize starch in spite of the considerably lower amylopectin content. More research needs to be performed to confirm this conclusion. The aging of starch is illustrated in Figure 8.5 for waxy maize and pea starch. As can be seen, moduli and tensile strengths increase, whereas the elongations decrease with time. The assumption is that the starch retrogrades further during storage. Recrystallized amylopectin acts as physical cross-links and increases the strength and decreases the elongation [15].

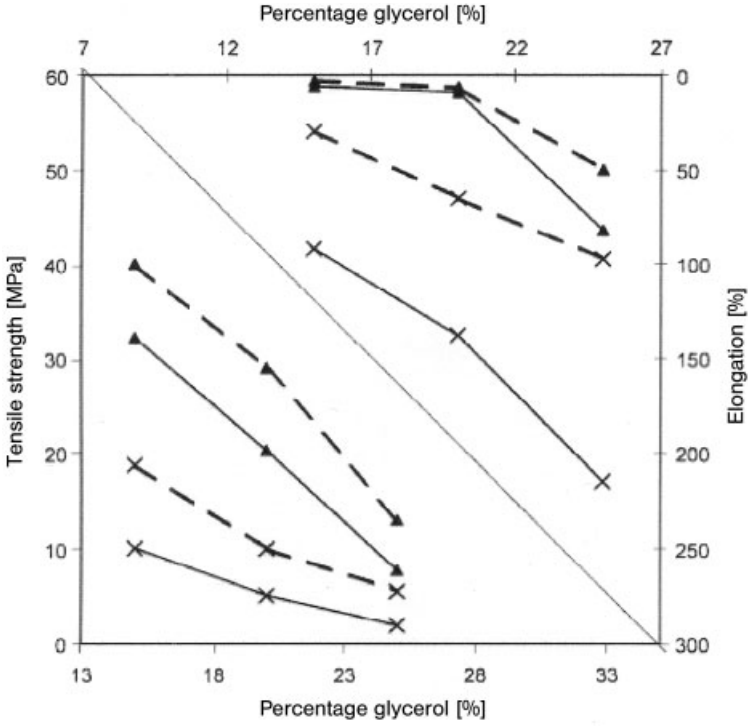

Figure 8.5 Aging of waxy maize (▲) and pea (×) starch reflected in the tensile strength and elongation after 1 day (—) and after 21 days (– – –) as a function of the glycerol content.

8.6 Impact Strength

As depicted in Figure 8.6, the impact strengths of all samples are very low and around the impact strength of PS. The T_g is lowered by glycerol, as would be expected from Equation 8.1, and this is of great importance for the impact strength. The T_g indicates the temperature above which the polymer can react through deformation; below the T_g it is a stiff and often brittle material. In our case the T_g values decrease, which means that the polymer toughness and impact strength should increase. There is a large difference in behavior on slow deformations as in the tensile tests with a movement of 10 mm per minute, and deformations on a short timescale, like the impact tests. Potato starch with 20% glycerol and a T_g of 57 °C, for instance, is very flexible, as is also illustrated by the elongation of 40% during the tensile tests, but nevertheless has a very low impact strength. The same phenomenon occurs for potato, wheat, and waxy maize starch with 25% glycerol and pea starch with 15, 20, and 25% glycerol. The assumption is that the broad

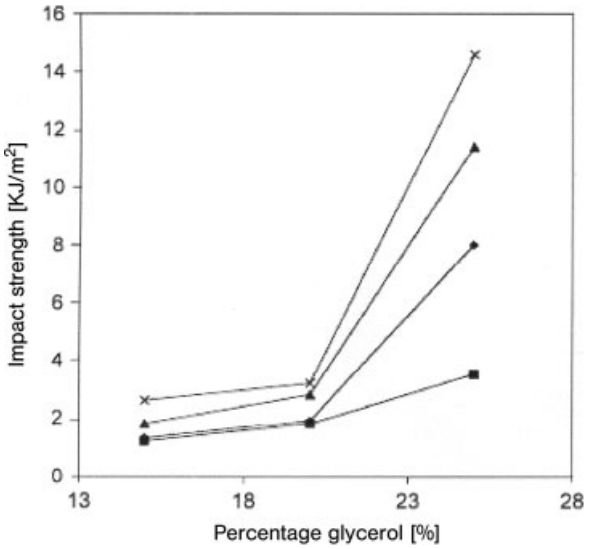

Figure 8.6 Impact strength of potato (♦), wheat (■), waxy maize (▲), and pea (×) starch as a function of glycerol content.

peaks of tanδ, generated by the DMTA tests, are the basis of this phenomenon. With a peak around 57 °C, the T_g of potato starch with 20% glycerol is far above the temperature of testing, which is 20 to 25 °C. However, tanδ is already increasing before the test temperature. With regard to the acclivity of tanδ there is a matter of limited mobility of the chains. This is apparently enough to distort the material during slow deformations, such as bending and the tensile tests, but deformations on a short timescale, such as impact tests, will cause a brittle fracture at this point.

8.7 Shrinkage

Sample bars made by injection-molding change in size during storage. In the injection direction there is obvious shrinkage, whereas in the direction perpendicular to it an increase in size is detectable. Figure 8.7 shows the results relating to the shrinkage of the sample bars after 1 week; no further shrinkage was measured after this period. At lower glycerol contents (15%) there is hardly any shrinkage of starch with a higher percentage of amylopectin, so it can be concluded that the chains need a certain amount of plasticizer, which enables the relaxation process. When the starch contains more amylose a lower amount of glycerol is necessary, due to the more mobile linear amylose chain. The injection of the polymer in the mold induces an elongation flow [16], and the chains of the polymers are consequently orientated in the injection direction. The chains are there-

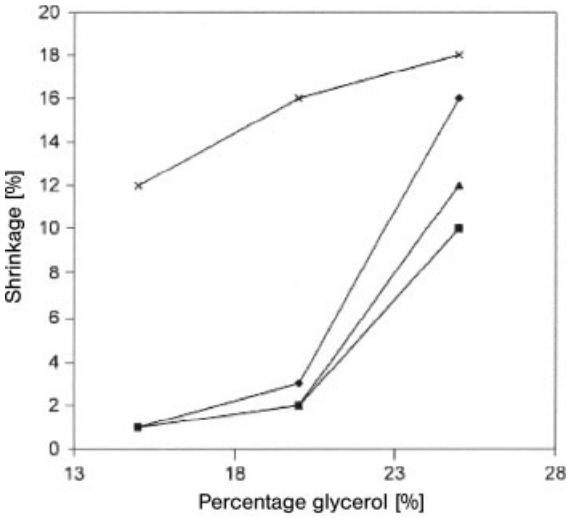

Figure 8.7 Shrinkage (in the injection direction) of injection-molded specimens after 1 week for potato (♦), wheat (■), waxy maize (▲), and pea (×) starch as a function of the glycerol content.

fore in a stretched conformation and lie parallel to each other. When the injection is stopped, reorientation starts and the chains realign in a helix configuration. This explains the shrinkage in the injection direction and the swelling in the width. Besides that, retrogradation will also cause shrinkage through the formation of hydrogen bonds between the chains with repulsion of water molecules. As would be expected, the shrinkage becomes faster with increasing glycerol fraction. This is due to the decreased local viscosity and the concomitant increased mobility of the chains, which make a faster relaxation possible. The shrinkage of waxy maize starch takes much more time than that of the other starches. The large proportion of amylopectin means that the chains are more entangled, which causes a lot of interactions and consequently a limited freedom to move relative to starch with higher amylose content. Finally it can be stated that the specimens made by pressing do not shrink to the same degree as the injection-molded specimens. During pressing there is no elongation flow present, resulting in less relaxation of the chains.

8.8 Conclusion

Addition of glycerol tends to reduce the glass transition temperatures of extruded starches and to narrow the transition regions. However, with glycerol contents of up to 25%, the T_g values are not lowered below 20 °C for the starches used. Lower

T_g values cause increases in impact strength, but with glycerol contents of 15 to 25% these increases remain quite low (up to 15 kJ m^{-2}). The moduli and tensile strengths decrease with glycerol content whereas elongations increase. The same effect is noticeable in the case of the amylose/amylopectin ratios of the starches: an increase in this ratio lowers the modulus and tensile strength and increases the elongation. Shrinkage of thermoplastic starch products made by injection-molding is considerable for those with glycerol contents above 20%. This shrinkage is caused by the elongation flows during injection.

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